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Narrowing the Range of Possible Solutions to the Pu Electronic Structure Problem: Developing a new Bremstrahlung Isochromat Spectroscopy Capability

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Abstract. Bremstrahlung Isochromat Spectroscopy (BIS) has a proven record for the probing of unoccupied electronic structure, including feasibility studies of actinides such as U and Th. A description of the BIS or Inverse Photoelectron Spectroscopy (IPES) process and of our reasoning concerning the potential importance of extending the application of BIS related techniques to the actinides, will be provided. To put this into the proper context, our past successes, using soft x-ray techniques to interrogate the electronic structure of Pu, will be briefly reviewed. Finally, the initial results of the calibration of the BIS device, including preliminary spectra from of the surrogate system CeOxide, will be presented.

1. The correlation between BIS results and unoccupied electronic structure of U

Baer and Lang have pioneered the application of BIS to number of systems, including actinides. [1] In particular, they have provided crucial spectra of U and Th, collected at higher energies. Our more recent calculations [2,3] demonstrate the strong agreement between the BIS experimental results and our theoretical density of states, especially the unoccupied electronic structure, as can be seen in Figure 1 below.

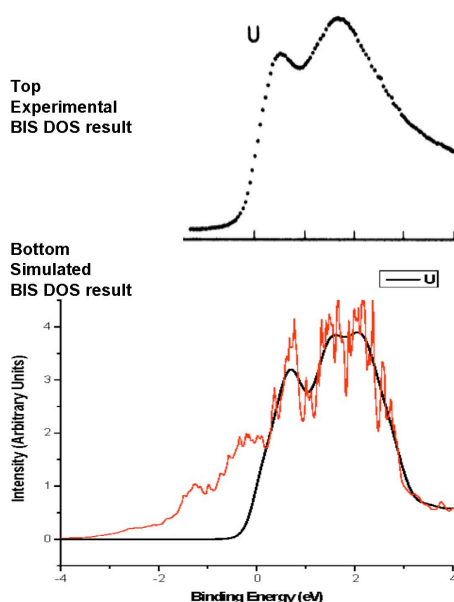


Figure 1

This is a comparison of an earlier BIS measurement by Baer and Lang [1] of Uranium with a simulated Density of States. The simulation is generated by starting with a calculation by Kutepov (in red), [3] which is truncated at the Fermi Energy (only unoccupied states can contribute to BIS) and then smoothed to reflect broadening from the instrumental band-pass (in black).[2]

Top: Experimental BIS result of Baer and Lang. [1]

Bottom: Red: DOS calculations by A.L. Kutepov; Black: DOS calculation times inverse Fermi function, with some instrumental broadening. [2]

2. Digression: Bremstrahlung Isochromat Spectroscopy and Inverse Photoemission

The central technique is BIS, or high energy Inverse Photoelectron Spectroscopy. [1,3,4,5] BIS is the high-energy variant of inverse photoelectron spectroscopy (IPES: electron in, photon out), which is essentially the time reversal of photoelectron spectroscopy (PES: photon in, electron out), as illustrated in Figure 2. Photoelectron spectroscopy is a widely utilized technique with multiple applications. (Please see References 6-8 and references therein.) However, the underlying event is always the same: (1) a photon impinges upon the sample and is absorbed; and (2) the energy passes to an electron, which is ejected. In the case of valence band photoelectron spectroscopy, one can either map the occupied band structure in angle resolving experiments upon single crystals or probe the occupied density of states (occupied DOS) by angle-averaging with polycrystalline samples, usually at higher energies. Generally speaking, IPES is the time reversal of the valence band PES, only now the unoccupied states (unoccupied DOS) are interrogated. (For metals with their short screening lengths, the inconsistencies due to differences in final state charges become negligible.) IPES can be used to follow the dispersion of unoccupied electronic states in ordered samples. [5] Owing to its low energies, IPES is usually very surface and band sensitive. However, by working at higher energies and using polycrystalline samples, we will sample preferentially for the bulk density of states, downgrading the impact of surface and band effects.

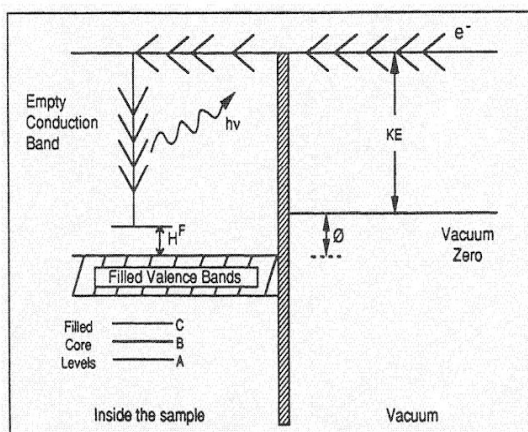


Figure 2

Shown here is a schematic of the inverse photoelectron process. KE is kinetic energy of the incoming electron, θ is the work function, H^F is the energy of the state relative to the Fermi Level, and $h\nu$ is the energy of the emitted photon. A defining characteristic of IPES/BIS is that $h\nu \approx KE$.

Thus, from BIS, we would argue that we should have a direct measure of the conduction band or unoccupied electronic structure of the bulk Pu. In support of this contention, we have presented the comparison shown above in Figure 1. Here, experimental BIS data from Baer and Lang [1] is directly compared to a simulated BIS spectrum generated from a calculation of the density-of-states of alpha-U. The match is excellent, strongly supporting the validity of this approach.

3. The Pu Enigma

Significant questions remain concerning the nature of Pu electronic structure. [3,4,6,7,9] While chemically toxic and highly radioactive, Pu may be the most scientifically interesting element in the periodic table. It's properties include the following: six different phases, close to each other in energy and sensitive to variations of temperature, pressure and chemistry; the face-centered-cubic phase (delta) is the *least* dense; Pu expands when it solidifies from the melt; and it is clearly the nexus of the actinide binary phase diagram of the actinides. In a sense, it is the boundary between the light (ostensibly delocalized 5f electrons) and heavy (ostensibly localized or correlated 5f electrons) actinide elements, but this is an over-simplification. The localized atomic 5f states are naturally correlated, but important regimes of correlated electron states are

conceivable as extended states on the delocalized side of the possible Mott transition. The proximity to this crossover may be the driving force behind all these exotic properties. Pu remains of immense technological importance and the advancement to a firm, scientific understanding of the electronic structure of Pu and its compounds, mixtures, alloys and solutions is a crucial issue.

Photoelectron Spectroscopy [6,7] and X-ray Absorption Spectroscopy [3,7,9] have contributed greatly to our improved understanding of Pu electronic structure. (See Figure 1.) From these and related measurements, the following has been determined.

1. The Pu 5f spin-orbit splitting is large.
2. The number of Pu5f electrons is 5.
3. The Pu 5f spin-orbit splitting effect dominates 5f itineracy.

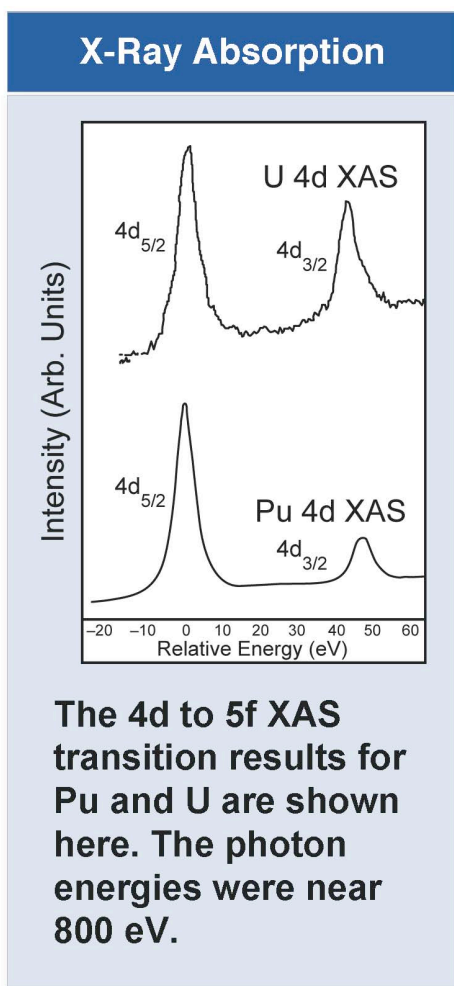


Figure 3

To the left, the X-ray absorption spectra (XAS) of alpha-U and alpha-Pu.

BIS and the unoccupied DOS

Perhaps the missing piece of the puzzle is the direct experimental determination of the unoccupied density of states (unoccupied DOS) using high energy inverse photoelectron spectroscopy (IPES) or Bremsstrahlung Isochromat Spectroscopy (BIS).

Moreover, while there are a number of ongoing experimental efforts directed at determining the occupied (valence band, below the Fermi Energy) electronic structure of Pu, there is essential no experimental data on the unoccupied (conduction band, above the Fermi Energy) electronic structure of Pu.

To this end, a new BIS capability [2,4,10] has been developed in our laboratory, which will be discussed next.

4. Experimental Instrumentation: Fano/BIS Spectrometer

A new Fano/BIS Spectrometer has been developed in our laboratory, as shown schematically in Figures 4 and 5 below. Fano Spectroscopy is a type of specialized photoelectron spectroscopy, which combines true spin detection with chirally configured excitation. [8] Under these conditions, it is possible to get detailed information concerning the interaction of spins and spin-orbit splitting, even within non-magnetic systems. The BIS capability is provided by the XES-350 monochromator/detector and an electron gun (not shown). (See Figure 4 caption for more detail.)

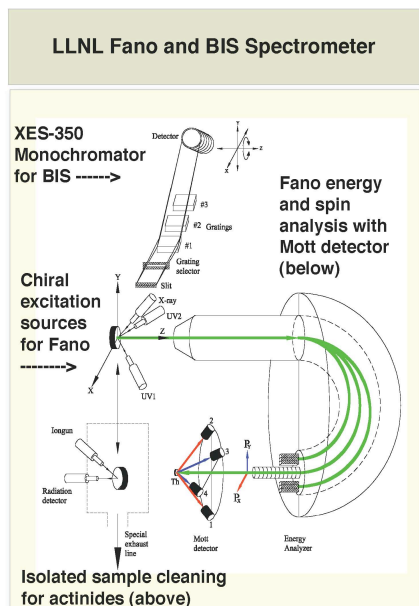
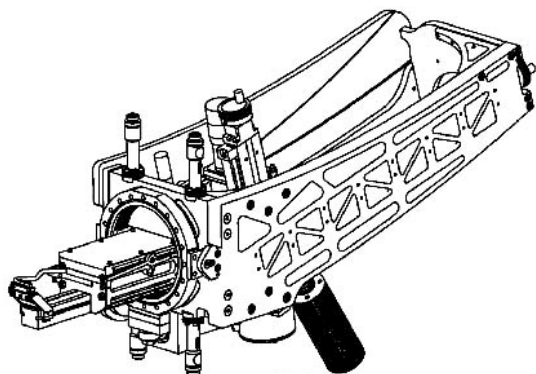


Figure 4 Caption

Sketch for BIS and spin resolved photoelectron spectroscopy (SRPES) experimental setup installed recently at Lawrence Livermore National Lab for the electronic structure study of actinides. For BIS, the detection of the photons is performed with the XES-350 monochromator and multi-channel detector.



BIS Photon Detection

Figure 5

A Schematic of the XES-350 monochromator and detector is shown here. Figure provided by Scienta.

The XES-350 uses three overlapping gratings to cover the energy range from below 100 eV to above 1000 eV. The image of the exit slit of the monochromator then falls upon a multichannel detector, which can be summed in the non-energy direction to provide energy dispersive spectra of the photon emission. In the case of IPES/BIS, the photon energy ($h\nu$) and kinetic energy (KE) are approximately equal. This is a demanding experiment, in which the cross sections are relatively low [1,5]. To aid in data collection in IPES/BIS, we have installed a new high current electron gun and are presently commissioning it.

5. BIS and XES results from CeOxide

As a preliminary test of the XES-350 system, a series of measurements have been performed upon oxidized, polycrystalline Ce. We have had substantial experience with Ce samples, including XAS [11] and Fano [8] measurements. XAS and related measurements, as well as theoretical spectral simulations for Ce are shown in Figure 6. [11] One advantage of permitting the oxidation of the Ce before the BIS measurements is the maximization of the number of holes in the Ce4f states and, thus hopefully, the BIS signal as well.

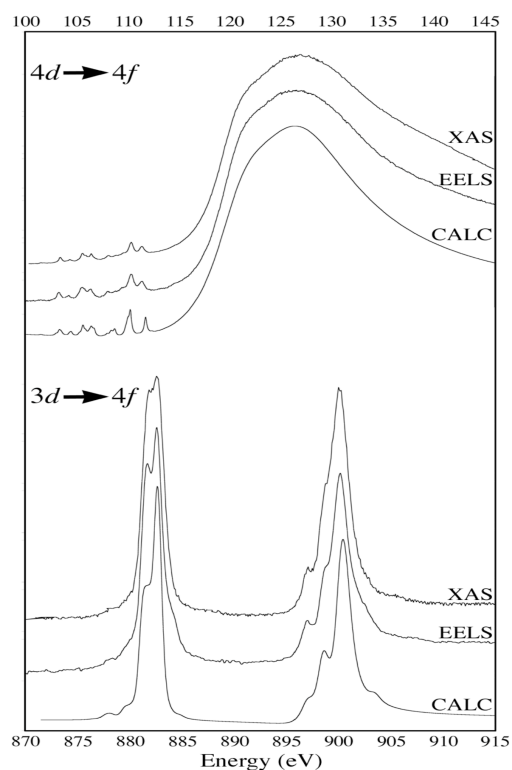


Figure 6
X-ray absorption spectroscopy (XAS), Electron Energy Loss (EELS) and spectral simulations for the 3d to 4f and 4d to 4f transitions in Ce. See reference 11 for details.

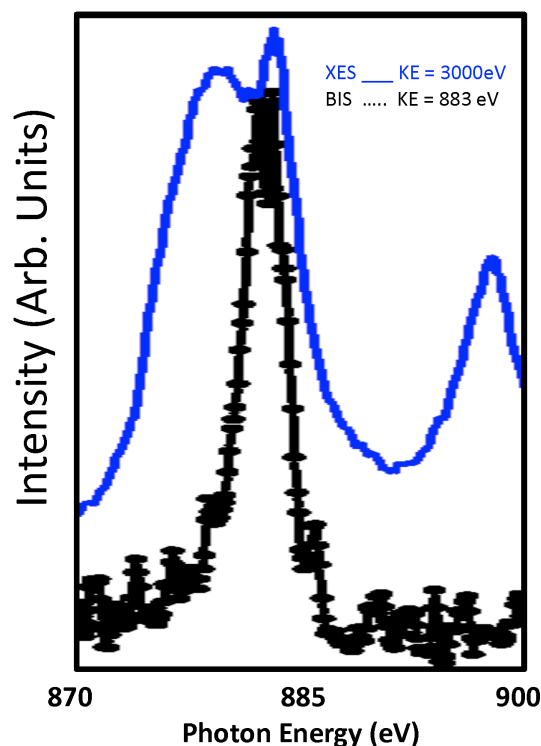


Figure 7
X-ray Emission Spectroscopy (XES) and Bremsstrahlung Isochromat Spectroscopy (BIS) of oxidized Ce. For XES, the excitation beam energy was 3000 eV. For BIS, the beam excitation beam energy was 883 eV. The total energy resolution in the BIS experiment is estimated to be approximately 1.5 eV.

X-ray Emission Spectroscopy (XES) is a generic name that includes BIS. However, the spectrum shown in Figure 7 correspond to core level XES. Here, a high-energy electron beam (3000 eV) is used to generate holes in the core levels. This would correspond to the levels A, B and C shown in Figure 2. Subsequently, a decay process can occur, where electrons in less tightly bound levels transition into the core hole. If the extra energy is transferred to an electron, Auger Spectroscopy is the result. If the extra energy is emitted as an X-ray photon, then XES is the result. If one were to substitute photonic excitation for electronic excitation, then this process would be called fluorescence or phosphorescence.

6. Summary

Briefly introducing the BIS of U from Baer and Lang [1] and summarizing our previous results, we have discussed the efficacy of BIS measurements as a means of determining the unoccupied DOS of Pu and resolving the Pu electronic structure controversy. Technical details and preliminary test results of the new BIS capability have also been presented.

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